## LETTER

# A simple inorganic process for formation of carbonates, magnetite, and sulfides in Martian meteorite ALH84001

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## ABSTRACT

We show experimental evidence that the zoned Mg-Fe-Ca carbonates, magnetite, and Fe sulfides in Martian meteorite ALH84001 may have formed by simple, inorganic processes. Chemically zoned carbonate globules and Fe sulfides were rapidly precipitated under low-temperature (150 °C), hydrothermal, and non-equilibrium conditions from multiple fluxes of Ca-Mg-Fe-CO<sub>2</sub>-S-H<sub>2</sub>O solutions that have different compositions. Chemically pure, single-domain, defect-free magnetite crystals were formed by subsequent decomposition of previously precipitated Fe-rich carbonates by brief heating to 470 °C. The sequence of hydrothermal precipitation of carbonates from flowing CO<sub>2</sub>-rich waters followed by a transient thermal event provides an inorganic explanation for the formation of the carbonate globules, magnetite, and Fe sulfides in ALH84001. In separate experiments, kinetically controlled <sup>13</sup>C enrichment was observed in synthetic carbonates that is similar in magnitude to the <sup>13</sup>C enrichment in ALH84001 carbonates.

### INTRODUCTION

The formation mechanism(s) for carbonates, magnetite, and sulfides in Martian meteorite ALH84001 remains a topic of great interest since McKay et al. (1996) reported that this orthopyroxenite meteorite might exhibit signatures for relict Martian life. Suggested formation temperatures for the chemically zoned Fe-Mg-Ca carbonate globules range from near 25 °C, which are favorable to life, to temperatures over 650 °C, which are not favorable (e.g., McKay et al. 1996; Romanek et al. 1994; Harvey and McSween 1996; Treiman 1995; Valley et al. 1997; Scott et al. 1998; Kirschvink et al. 1997; Gleason et al. 1997; McSween and Harvey 1998; Warren 1998; Leshin et al. 1998; Golden et al. 2000). The presence of single-domain, chemically pure, parallelepiped-type magnetite crystals and Fe sulfides in the rims of the globules is central to the argument for relict life (McKay et al. 1996; Thomas-Keprta et al. 2000a), but others argue that these magnetite crystals and Fe sulfides are not unique markers for life, but are produced by inorganic processes (e.g., Bradley et al. 1996). We have previously shown experimental evidence that the zoned carbonate globules in ALH84001 can form inorganically by precipitation under mild hydrothermal conditions (150 °C) from Ca-Mg-Fe-CO<sub>2</sub>-H<sub>2</sub>O systems (Golden et al. 2000). Brearley (1998) suggested that the single-domain magnetite in ALH84001 formed by the thermal decomposition of siderite or Fe-rich carbonate in association with shock heating and formation of maskelynite, which is found in association with the carbonate. By combining precipitation and heating steps, we have found that simple inorganic processes can explain the carbonate/magnetite/Fe-sulfide assemblage in ALH84001.

#### METHODS

A multiple step precipitation process was used to produce chemically and mineralogically zoned synthetic carbonate globules, i.e., the one-step procedure of Golden et al. (2000) was replaced by a four-step procedure. In each step (Table 1), appropriate cations (Ca, Fe, and Mg) in the form of chloride salts were dissolved in deoxygenated CO<sub>2</sub>-saturated water. Next, NaHCO<sub>3</sub> was added as a pH buffer while CO<sub>2</sub> was passed continuously through the solution (Table 1). A 15 mL aliquot of the solution was transferred into a 20 mL Teflon-lined hydrothermal pressure vessel. Hydrothermal vessels were closed in a CO2-atmosphere and transferred into an oven at 150 °C. After a predetermined time (Table 1), hydrothermal vessels were removed from the oven and quenched in a freezer. Supernatant solutions were decanted and carbonate precipitates were washed free of soluble salts by repeated decantations with deionized water. The same procedure was used for each subsequent step, except that the solution was added to the washed carbonate precipitate from the previous step in the hydrothermal vessels (see Table 1 for the mineralogy of precipitates after each step). Sulfur was included in the second and fourth steps to form Fe sulfides (i.e., pyrite) in addition to siderite (see Table 1). Thus, the chemically zoned globules consisted of an ankeritic core (step 1) followed by concentric zones of siderite + pyrite (step 2), magnesite (step 3), and siderite + pyrite (step 4).

To simulate a transient thermal event in the meteorite, the synthetic globules were heated to and cooled from 470 °C in a differential scanning calorimeter (DSC) at the rate of 20 °C/ min (i.e., a rapid, controlled-heating event) in a stream of  $CO_2$  at 13.3 kPa (step 5). Heating converted the siderite + pyrite to magnetite + pyrrhotite and left the ankerite and magnesite virtually unaffected. The final, heated products (after step 5) were

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	Starting solution compositions (mmoles)*					Vol. Time	Cumulative Run Products (by XRD†)	
	Ca	Fe	Mg	NaHCO <sub>3</sub>	S	(mL)	(h)	
Step 1	0.45	0.3	1.8	3.0	0	15	7	ankerite
Step 2	0	1.5	0	1.5	0.16	15	1	ankerite, siderite, pyrite
Step 3	0	0	1.8	3.75	0	15	10	ankerite, siderite, pyrite, magnesite
Step 4	0	1.5	0	1.5	0.16	15	1	ankerite, siderite, pyrite, magnesite
Step 5	Heat at 20 °C/min to 470 °C in CO <sub>2</sub> at 13.3 kPa							ankerite, magnetite, pyrrhotite, magnesite

 
 TABLE 1. Synthesis steps, experimental conditions and starting solutions, and cumulative run products from the synthesis of mineralogically and chemically zoned globules

Note: In steps 1–4, starting solutions (and solids from the previous synthesis step, if applicable) were placed in Teflon-lined hydrothermal vessels and heated to 150 °C.

\* Starting solutions (mmoles in 15 mL) were made from reagent grade CaCl<sub>2</sub>, FeCl<sub>2</sub>, MgCl<sub>2</sub>, NaHCO<sub>3</sub>, and elemental sulfur.

+ XRD = X-ray diffraction analysis.

globules that contained ankeritic cores and concentric zones of magnetite + pyrrhotite, magnesite, and magnetite + pyrrhotite. Chemical and mineralogical properties of synthetic prodsis. All carbon isotope data are reported relative to the VPDB standard.

# **RESULTS AND DISCUSSION**

ucts were characterized by a combination of analytical techniques. A Scintag XDS 2000 X-ray diffractometer using CuKa radiation was employed to determine the mineralogical composition of non-oriented synthetic globules. For field emission scanning electron microscopy (FESEM) and electron microprobe analysis (EMPA), carbonate spheres were embedded in Buehler thin-section epoxy, after which they were polished using carborundum papers, diamond lapping film disks, and alumina. Polished sections were coated with 5 nm of carbon using a Gatan high-resolution ion beam coater. Coated thin sections were examined with a JEOL 6340F+ field emission scanning electron microscope equipped with an IXRF energydispersive X-ray spectroscopy (EDS) system. Analyses were conducted using a 15 kV accelerating voltage and a 12 µA emission current. Synthetic carbonate globules that had been embedded in epoxy, thin sectioned, and carbon coated were also chemically analyzed by EMPA on a Cameca SX100 electron microprobe using well-characterized minerals as standards. Polished thin sections of carbonate globules in Martian meteorite ALH84001 were analyzed by EMPA and EDS for comparison with synthetic carbonate globules. A few hundred particles of freeze-dried carbonates were embedded in Embed 812 epoxy on a precast epoxy block for transmission electron microscopy (TEM) analysis. The embedded area was trimmed to a trapezoid shape and cut into ~70 nm thick sections using a diamond knife mounted on an RMC MT-7000 ultra microtome. Sections were collected using a copper grid with carbon-coated formvar substrates and examined under a JEOL 2000FX scanning transmission electron microscope operated at 160 or 200 kV.

For the carbon isotopic studies, carbonates were synthesized separately using each step in Table 1 to yield monomineralic carbonates corresponding to the zones in the globules. A single source of CO<sub>2</sub> gas was bubbled through the pH-adjusted brine (adjusted with 1 *M* NaOH) to generate bicarbonate, until an equilibrium pH of ~6.3 was achieved. The resultant solution was heated to 150 °C to obtain single-phase carbonates. Carbon isotope measurements were performed on carbonates precipitated at 150 °C and on samples heated further to 470 °C as outlined in Table 1. Samples were measured for carbon isotope composition by reaction with 100 % orthophosphoric acid. The CO<sub>2</sub> was extracted and analyzed on a Finnigan Delta "S" mass spectrometer, which was modified for continuous flow analy-

The similarity between our synthetic globules and those of ALH84001 is striking (Fig. 1). Chemical compositions of the synthetic globules are illustrated by EDS element maps in Figure 1a; the corresponding mineralogical identifications are based on XRD analyses. The core shows a Ca-Fe rich carbonate center grading outward to more Mg-rich carbonate. The adjacent zone is Fe-rich with traces of S, which is indicative of magnetite + pyrrhotite (originally siderite + pyrite before heating). The next zone outward is very Mg-rich, indicating nearly monomineralic magnesite. The outermost zone (rim) is Fe and S rich, again indicating the magnetite + pyrrhotite rims (not shown). This sequence of zones in our synthetic globules, including the magnetite + pyrrhotite assemblage in the rim, is similar to the globules in ALH84001 (Fig. 1b).

The diameter range of fully developed globules was 10-80 µm. Most globules were spherical with a saw-toothed outer contour resulting from the relatively well-crystallized nature of the magnesite rim. This morphology is very similar to that reported for the ALH84001 globules (e.g., McKay and Lofgren 1997). The magnetite + pyrrhotite rims are visible as bright bands in backscattered-electron images (Fig. 1a). When orthopyroxene was added as a nucleation substrate in the synthesis, pancake-shaped globules formed within cracks and hemispherical globules along surfaces of the pyroxene (Fig. 2a) in a fashion very similar to the "pancake-shaped" globules in ALH84001 (Fig. 2b). The transient nature (i.e., short duration) of the carbonate precipitation process and minimal alteration of the orthopyroxene in our experiments agree well with previous experimental studies that suggest ALH84001 experienced limited interactions with aqueous fluids (Baker et al. 2000; Golden et al. 2000).

The carbon isotopes of ALH84001 carbonates yield clues to their formation. Carbon isotope analyses of single-phase ankerite, siderite, and magnesite that we synthesized hydrothermally (non-equilibrium conditions) using the same source of CO<sub>2</sub> were all enriched in <sup>13</sup>C compared to the starting CO<sub>2</sub> (Table 2). This enrichment results from the combined effects of kinetic-isotope fractionation during precipitation and thermal decomposition and is not an equilibrium fractionation. The 10.4 to 13.9 ‰ enrichment of <sup>13</sup>C during these combined processes is much greater than that expected from equilibrium frac-



**FIGURE 1.** Backscattered-electron image and elemental X-ray maps: (a) experimentally produced globules; and (b) carbonate globule in Martian meteorite ALH84001 (bse = backscattered-electron image; Mg = magnesium X-ray map; Ca = calcium X-ray map; Fe = iron X-ray map; S = sulfur X-ray map). In synthetic globules, the surrounding medium is epoxy, which is free of Ca, Fe, Mg, and S. In ALH84001, the background is feldspathic glass and orthopyroxene (opx).

tionation (e.g., Friedman and O'Neal 1977). The enrichment of <sup>13</sup>C in ALH84001 carbonates with respect to the Martian atmosphere is on the order of 12.5 to 14.8 ‰ (Romanek et al. 1994; Hartmetz et al. 1992). The correspondence of the <sup>13</sup>C enrichment between our synthetic carbonates and those in ALH84001 carbonates suggests that inorganic processes can explain the large positive  $\delta^{13}$ C shift for the ALH84001 carbonates.

TEM images of the synthetic globules reveal details of the

relationship of the carbonates and the magnetite + pyrrhotite assemblage (Fig. 3). Two magnetite-containing bands sandwich the magnesite zone (Fig. 3a). The shape and size of the magnetite formed by the decomposition of Fe-rich carbonates are nearly identical to magnetite that occurs in rims of ALH84001 carbonate globules (McKay et al. 1996). Our thermally produced magnetite crystals are predominantly 10–100 nm in diameter, in the superparamagnetic to single-domain size range (Butler and Banerjee 1975), chemically pure, free of lattice



**FIGURE 2.** Field emission gun scanning electron micrographs in backscattered-electron mode: (a) experimentally produced carbonate globules exhibit a "pancake-type" morphology that have formed in cracks of orthopyroxene (opx); and (b) carbonate globules that have formed in cracks and voids of Martian meteorite ALH84001.

TABLE 2.	Carbon isotopic composition ( $\delta^{13}C_{VPDB}$ ) of synthetic car							
	bonates and Martian carbonates in the ALH84001 me							
	teorite							

	Ankerite (‰)	Magnesite (‰)	Siderite (‰)				
	Synthetic Carbonates						
Source CO <sub>2</sub>	$-33.48 \pm 0.08$	$-33.48 \pm 0.08$	$-33.48 \pm 0.08$				
Hydrothermal	$-26.57\pm0.09$	$-22.76\pm0.07$	$-24.95 \pm 0.07$				
Hydrothermal synthesis	$-23.04\pm0.08$	$-21.40\pm0.05$	$-19.56 \pm 0.31$				
<sup>13</sup> C-enrichment	10.44	12.08	13.92				
	ALH84001-Carbonate Zones						
Mars Atmosphere*	$27.0 \pm 0.4$	$27.0 \pm 0.4$	NA†				
ALH84001-Carbonate‡	39.5	41.8	NA				
<sup>13</sup> C-enrichment	12.5	14.8	NA				

\* The carbon isotope composition of the Martian atmosphere is poorly constrained. The numbers cited here were adopted from the measured values of Hartmetz et al. (1992).

† Not applicable.

‡ Romanek et al. (1994)

defects (Fig. 3b), and present in a number density that is large compared to magnetite precipitated directly from solution.

In-situ chemical analysis of single magnetite or sulfide crystals in thin-sectioned samples was difficult because of their small diameters. Therefore, we analyzed a large number of chemically extracted magnetite grains (carbonates removed by treatment with 20% acetic acid at 50 °C for ~72 h followed by centrifuge washing) by analytical electron microscopy. The magnetite grains are chemically pure as only Fe was detected, possibly because other elements (e.g., Cr, Ti, and Mn), which commonly substitute in the magnetite structure, were not present in our solutions. However, Mg, which is in our solutions and forms a spinel mineral (MgFe<sub>2</sub>O<sub>4</sub>, magnesioferrite), is not present as a detectable impurity.

The shape of the magnetite particles is variable and includes cuboid, teardrop, tooth, parallelepiped, hexagonal, irregular (Figs. 3c,d,e), and whisker (not shown) shaped particles. Although different magnetite shapes were observed, the factors that control shape and the frequency distribution of each shape were not investigated. We also have not performed a detailed comparison of crystallographic morphologies of our synthetically produced magnetite grains to magnetite produced by magnetotactic bacteria (Bazylinski et al. 1997); crystallographic morphology has been argued as a key diagnostic for biogenically produced magnetite (Thomas-Keprta et al. 2000b). Nevertheless, our synthetic magnetite grains duplicate all of the shapes reported for ALH84001 magnetite grains.

Although an S-bearing phase was detected in the magnetite rims from EDS analysis (Fig. 1a, S image), we could not make a mineralogical identification by TEM. Pyrrhotite was identified by XRD analysis, so the S-bearing phase in the magnetite rims is likely pyrrhotite. Pyrrhotite was the only sulfide phase identified in the magnetite rims of carbonates in ALH84001 (McKay et al. 1996). Under reducing conditions conducive to the formation of Fe sulfide and as observed in our experiments, coprecipitation of sulfide and carbonate is thermodynamically favored along the siderite-pyrite phase boundary (Garrels and Christ 1965). Thus, our experiments provide a means (coprecipitation of siderite and pyrite followed by thermal decomposition) of accounting for the magnetite-pyrrhotite assemblage observed in ALH84001.

We have simulated geological events that plausibly affected the host rock on Mars in our synthesis of ALH84001-like globules. In our model, the carbonate globules in ALH84001 first formed as a hydrothermal precipitation product from CO<sub>2</sub>-rich fluids whose composition changed with time and temperature,



**FIGURE 3.** Transmission electron micrographs (TEM) of experimentally produced globules: (**a**) overall view of the rim region showing an outermost 200 nm thin rim of magnetite-sulfide, a magnesite (Mag) zone, an inner magnetite+sulfide zone, and an innermost ankerite (Ank) core (see Fig. 4 in McKay et al. (1996) for comparison with ALH84001); (**b**) high resolution TEM image of a defect-free magnetite crystal produced by thermal decomposition of siderite (magnetite (111) lattice fringes = 4.8 Å); (**c**) TEM image (reverse contrast) of magnetite produced by thermal decomposition of siderite; parallelepipeds (pp), cubes (cb), and octahedra (oh); (**d**) TEM image (reverse contrast) of magnetite produced by heat decomposition of siderite; tooth shaped (th) and bullet shaped (bt); and (**e**) TEM image (reverse contrast) of a chain of magnetite grains produced by thermal deposition of siderite and illustrating tear-drop (td) shaped magnetite.

producing globules with ankeritic cores and concentric zones of Fe-rich carbonate (siderite) plus Fe sulfide (pyrite), magnesite, and another Fe-rich carbonate plus Fe sulfide. In terrestrial environments, hydrothermal precipitation of zoned siderite and ankerite from  $CO_2$ -rich fluids of fluctuating compositions (e.g., Fe, Ca, and Mg) has been reported in basaltic rocks from the Galapagos spreading center (Laverne 1993). Zoned carbonates of similar composition have also been reported in greenschist facies metamorphic rocks of the Esplanade Range and Northern Dogtooth Mountains, British Columbia (Jones and Ghent 1971) and in mantle xenoliths and basalts from Spitsbergen, Norway (Treiman et al. 1998). During a subsequent thermal event initiated by impact (e.g., Brearley 1998) or volcanic events, the ALH84001 globules were sufficiently

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heated to form magnetite and pyrrhotite as decomposition products of siderite and pyrite, respectively. An impact-induced transient heating event is favored by the putative impact history of the host rock during which multiple brecciation events were separated by periods of annealing (McKay et al. 1996; Ash et al. 1996; Treiman 1998). Impacts also may have formed the fractures and shattered zones in the rock that originally allowed the hydrothermal fluids to penetrate the rock. Because the ankerite and magnesite did not decompose in our experiments, we constrain the upper temperature limit for the thermal event to be ~475 °C at a pressure of 13.3 kPa CO<sub>2</sub>, which is the decomposition temperature for siderite, but not ankerite (>500 °C) and magnesite (>600 °C) as determined in separate experiments. The presence of some magnetite in the carbonate matrix of ALH84001 (McKay et al. 1996) may suggest that the meteorite experienced temperatures slightly above the onset of siderite decomposition (i.e., >475 °C under the conditions of our experiments), which converted some of the Fe-rich ankerite into magnetite. Another possibility is that these magnetite grains in ALH84001 carbonates may have precipitated directly from solution during the formation of the ankerite phase, similar to what we observed in some of the ankeritic cores of synthetic globules (data not shown). The thermal stability of carbonates is dependent upon the total pressure and CO<sub>2</sub> partial pressure (Lauer et al. 2000), and the carbonates might also have been affected by the duration of the heating event (e.g., short-lived, overstepping thermal pulse as described by Brearley 1998). Therefore, it is difficult to place precise constraints on the temperature of siderite decomposition in ALH84001.

In summary, we have reproduced, by simple inorganic processes, the chemical and mineralogical features of the carbonate-sulfide-magnetite assemblage reported by McKay et al. (1996) in ALH84001. Although the possibility of biogenic influence in the formation of the ALH84001 carbonate globules cannot be ruled out, our experiments suggest a plausible inorganic alternative for their formation.

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